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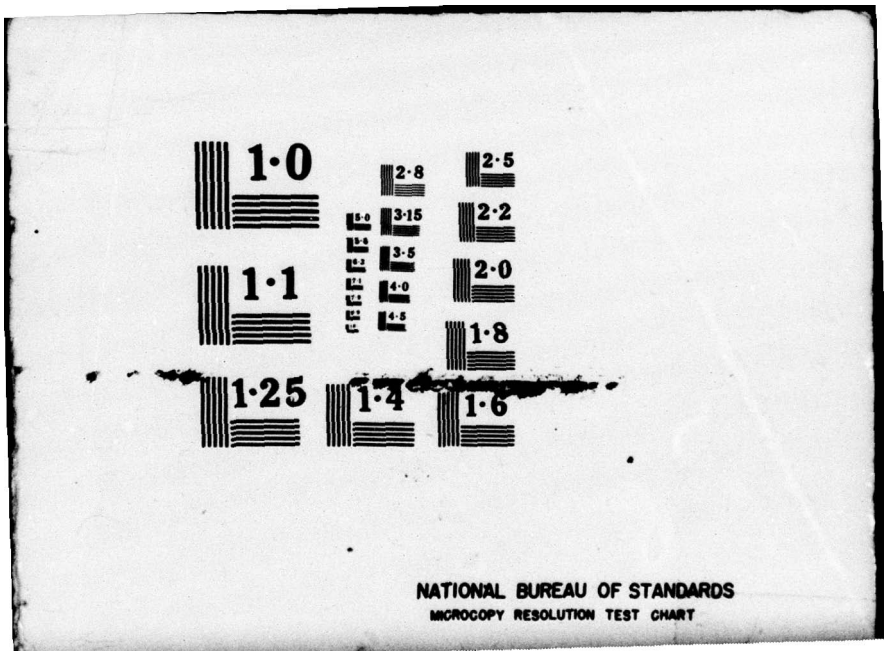
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SOLID STATE COEXTRUSION: A NEW TECHNIQUE FOR ULTRADRAWING THERMOPLASTICS ILLUSTRATED WITH HIGH DENSITY POLYETHYLENE

by

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Abstract

Ultra-oriented high density polyethylene (HDPE) extrudates have been prepared in continuous lengths by a new method employing conical dies of nominal draw ratios up to 36X. Preformed HDPE billets ~ 7 cm (DuPont Alathon 7050, M_w = 59,000, M_n = 19,900) were split longitudinally into two halves and then one or more wafers of the same polymer were inserted between the two sheath halves. Thereafter, the whole assembly was extruded in the absence of lubricant and at temperatures substantially below the melting range and afforded continuous and transparent films. The physical and mechanical properties of the HDPE films so produced were evaluated and compared with the respective properties of the same polymer extruded conventionally through a slit die. The high melt transitions, tensile modulus and transparencies confirm the effectiveness of the new method in obtaining continuous ultradrawn films.

Introduction

Polyethylenes and other semicrystalline thermoplastics have been ultraoriented by several means including solid state extrusion[1-5]. The prior limitations of extrusion for semicrystalline polymers below their melting points have prohibited attainment of: (1) high extrusion draw ratios, > 20; (2) fast extrusion rates; (3) continuous production of uniform and high draw; and (4) preparation of ultra-thin films and filaments. The extrusion draw ratio is defined as the ratio of the inlet to the outlet cross-sectional area of the extrusion die.

In this communication we report a new solid state extrusion technique, illustrated with high density polyethylene, which overcomes all the limitations of cold extrusion listed above. Conventionally, a semi-crystalline polymer has been extruded as a solid plug or billet through wedge-shaped or conical dies. The new technique involves the cold extrusion of longitudinally-split billets through a conical die only. A film strip has also been interposed within the split prior to extrusion. This process involving a split we call stress-relieved extrusion (SRE). A salient feature of the new technique is that either films or filaments may be ultradrawn at much faster rates and at relatively lower temperatures, pressures, and in the absence of lubricants. Ultradrawn films and filaments are formed, respectively, by inserting between the split billet low orientation films and filaments prior to extrusion. Thus, the new solid state coextrusion technique allows, for the first time, continuous production of unflawed film strips and filaments having extrusion

draw ratios of > 30X. Moreover, the process appears to efficiently orient and elongate the polymer chain at least for the illustration here of high density polyethylene films. Of course, coextrusion is an old metallurgical technique well documented in the literature[6]. In the present paper, however, the emphasis is on a new coextrusion method for ultra-drawing thermoplastics.

Materials and Methods

High density polyethylene (HDPE) (DuPont A7050R, M_w = 59,000, M_n = 19,900) were compression molded in vacuo at 160°C and under ~ 1300 atm in a special apparatus[7]. The billets were split longitudinally into two halves. A film strip of the same polymer, same morphology, and of the geometrical profile of the billet was imprinted with a 0.25 cm square grid pattern in order to measure the extent of draw and to observe the flow lines on extrusion. The film strip was then inserted between the two sheath halves as shown in Figure 1. The whole assembly was press-fitted into the reservoir of an Instron Capillary Rheometer maintained at the desired extrusion temperature. The split billets with the wafer sandwich were extruded through conical brass dies previously developed in our laboratory for the extrusion of ultra-drawn filaments of high density polyethylene[8]. The conical dies had an included entrance angle of 20° and a capillary length of 0.12 cm.

Two basic extrusion experiments were conducted to test the effect of the split billet. In the first experiment, a film strip of lower draw ratio (12X) was desired. For this, a 0.14 cm-thick wafer in the split billet was extruded at 110°C under a constant pressure of 0.10 GPa through a die with a capillary diameter of 0.278 cm. In the second experiment, in

which a film strip of higher draw ratio (36X) was desired, a 0.16 cm thick wafer was extruded at 120°C and 0.23 GPa through a die with a capillary diameter of 0.172 cm. For comparison, film strips were also prepared by conventional slit die extrusion at 134°C and 2400 atm. The stainless steel slit die had an initial entrance wedge with 33.4° included angle followed by a second wedge with 14.2° included angle at the narrow end of the slit. The entrance width of the wedge decreased from 0.8 cm to a final width of 0.045 cm over a distance of 2.8 cm. The film width was 0.415 cm. No lubrication was used in any of these extrusion experiments. Indeed the billets, dies, and rheometer reservoir were cleaned with acetone in order to remove any traces of lubricant prior to extrusion.

The effectiveness of the split billet technique to produce efficient drav was evaluated by physical and mechanical tests on the extruded film strips. Melting behavior was examined with a Perkin-Elmer DSC, Model 1B. Percent crystallinity values were determined from heat of fusion data, assuming a fusion heat for a perfect polyethylene crystal of 69 cal/g[6]. The total birefringence was measured with a Zeiss polarizing microscope equipped with an Ehringhaus compensator. An Instron strain-gage extensometer (10 mm gage length) was used in the tensile modulus measurements on the film strips. The strain rate was 3.3×10^{-4} sec^{-1}. The tensile modulus was determined from a tangent to the stress-strain curve at a strain level of 0.1%.

Results and Discussion

Upon being forced through the conical die, the split billet plus wafer assembly yielded an extrudate whose split components were highly compressed together.

The low extrusion temperatures substantially below the ambient melting point precluded any interfacial bonding via melting of the drawn components. Figure 2 shows that the extrudate could be easily delaminated longitudinally to yield a drawn thin film and two semiperipheral drawn billets. The billet components maintained positional integrity upon extrusion; there was no suggestion of buckling, twisting or migration of the drawn components.

To test the effectiveness of the split billet process as a function of draw, we measured the draw ratio (from grid extension) and tensile modulus at selected points along a 140 cm long film strip extruded at 120°C and 0.23 GPa in the die with 0.172 cm diameter. Figure 3 shows the variation of draw ratio and modulus along the initial portion of the film strip which arises from the volume reduction of the entrance cone[8]. In previous work[8,10] it has been difficult, particularly in extreme draw experiments, to deplete the entrance cone volume and extrude from the full billet diameter to achieve steady state production of extrudate (film or filament) with high and constant draw ratio and modulus. In contrast, in the split billet process, after the cone volume is emptied at a corresponding film length of about 28 cm, the draw ratio and modulus remain constant at about 30X and 28 GPa, respectively, until the entire split billet is exhausted from the rheometer reservoir. The slit-extruded film prepared from the solid billet, even at 134°C temperature, fractured at a low extrusion draw ratio of about 16.

Another important feature of extruding a split billet is the greatly-enhanced extrusion rate that is achieved. For example, for a split billet with wafer extrusion of the 11X

film at 110°C/0.10 GPa, the steady state extrusion rate was 16 cm/min. On the other hand, the extrusion rate during solid billet slit extrusion of a film of comparable draw ratio at 134°C/0.23 GPa was only 3 cm/min. Table 1 shows that the physical and mechanical properties of film strips prepared by the two techniques are comparable at equivalent draw ratio. The conventional slit extrusion was done at 134°C since extrusion did not occur at the lower temperatures of 110 and 120°C which readily facilitated the SRE method. Like the slit-extruded films, the films extruded by the split billet technique are transparent to visible light. Furthermore, the high melting points, birefringence values, and tensile moduli document the drawing effectiveness of the new technique. The birefringence of the 30X film is among the highest reported for high density polyethylene and in the range estimated for perfectly aligned crystals[11-13].

Uses, modifications, and variations of the stress-relieved extrusion concept are presently without bounds. The method is likely applicable generally to thermoplastics. Initially, the technique has been used to prepare highly anisotropic, ultra-thin (< 0.1 mm thick) films for use in light scattering and infrared dichroism studies. To alter film thickness, one need only change the initial wafer thickness and/or the capillary diameter.

The new solid state coextrusion technique has also been used to extrude simultaneously several films in one experiment by simply splitting the billet into several longitudinal wafers. Furthermore, the split-billet concept has been successfully extended to cylindrical geometries. Ultradrawn sheath-core filaments of high density polyethylene have been also continuously extruded at relatively low temperatures and pressures. In this case, the preformed billet for solid state coextrusion was made by placing a polymer rod within a tubular billet.

The mechanism and applications of stress-relieved extrusion are presently under study. The former is being investigated by studying the flow profiles of the imprinted grid lines. Importantly the results indicate that the operation of an extensional velocity field in contrast to the shearing deformation which is observed in conventional solid-state extrusion, even in dies of small entrance angle. A qualitative and tentative explanation is that the creation of longitudinal free surface areas within the polymer billet effectively changes and relieves the stresses which normally develop during extrusion of a conventional, unsplit billet. Under comparable extrusion conditions, a split billet always extrudes at a much faster rate than an unsplit billet. Furthermore, the SRE process can be achieved under conditions of pressure and temperature at which conventional solid-plug extrusion does not occur.

Conclusion

Stress-relieved extrusion offers a heretofore unexplored approach to the problems of solid state deformation of polymers in contained geometries. The technique has profound advantages and these are listed below:

1. It is more rapid, continuous and reproducible.
2. It requires only moderate processing pressures.
3. The process operates without the requirement of lubricant or a second liquid (hydrostatic mode).
4. It is a very convenient technique since it allows the preparation of continuous films or filaments using the same conical die.

In addition, the technique promises wide application. It is highly efficient in producing continuous lengths of films or filaments. It allows the preparation of extremely thin films and filaments. In this process of solid state co-extrusion, the components, even for different composition and molecular weights, extrude with integrity and at the same rate.

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Acknowledgment

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TABLE 1

Comparison of Properties of High-Density Polyethylene Film Strips Prepared by Slit-Extrusion and Split-Billet Extrusion

Property	Conventional Slit-Extrusion at 134°C, 0.23 GPa	Split-Billet Extrusion at 110°C, 0.10 GPa	Split-Billet Extrusion at 120°C, 0.23 GPa
Thickness, cm	0.045	0.045	0.032
Draw Ratio	11X	11X	30X
Visual Appearance	Transparent	Transparent	Transparent
Melting Point, °C[a] °C/min	140	140	141
Crystallinity, %	80.2	79.4	86.1
Birefringence	0.058	0.058	0.061
Tensile Modulus, GPa	7.9	7.1	28.1

[a]DSC heating rate = 10°C/min.

Captions for Figures

1. Schematic of split-billet assembly.

2. Photograph of delaminated filament extruded from a split-billet assembly.

3. Draw ratio and tensile modulus as a function of axial position along a film strip prepared by stress-relieved extrusion at 120^{o}C and 0.23 GPa.

SPLIT BILLET

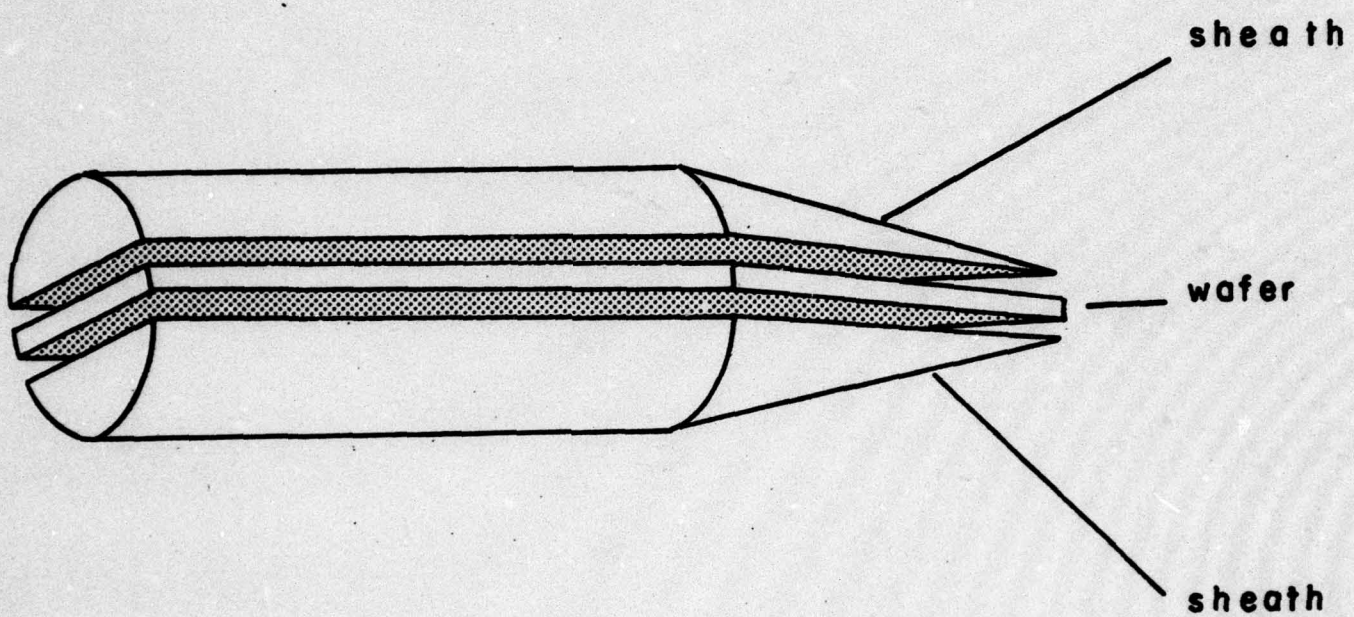


Figure 1

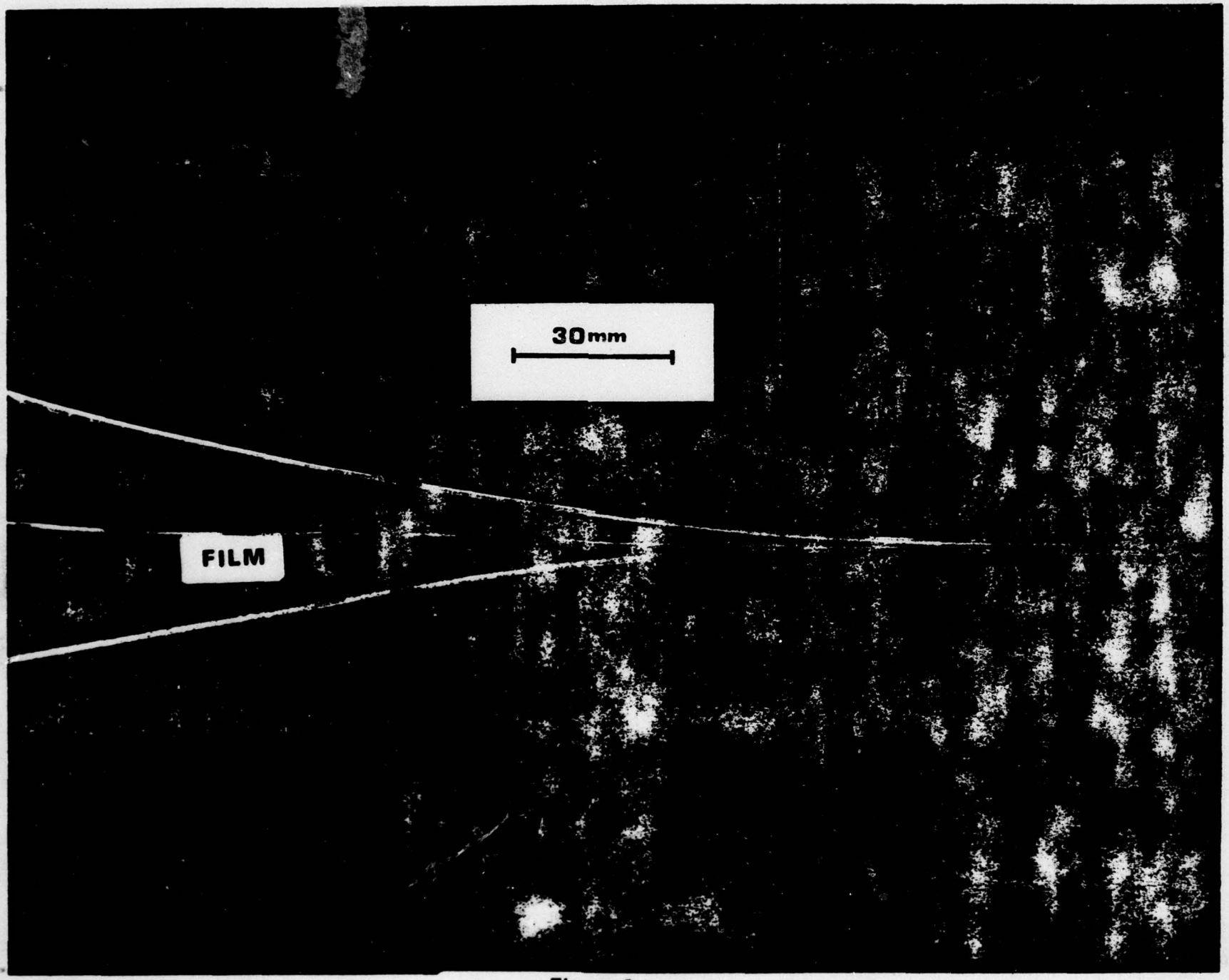
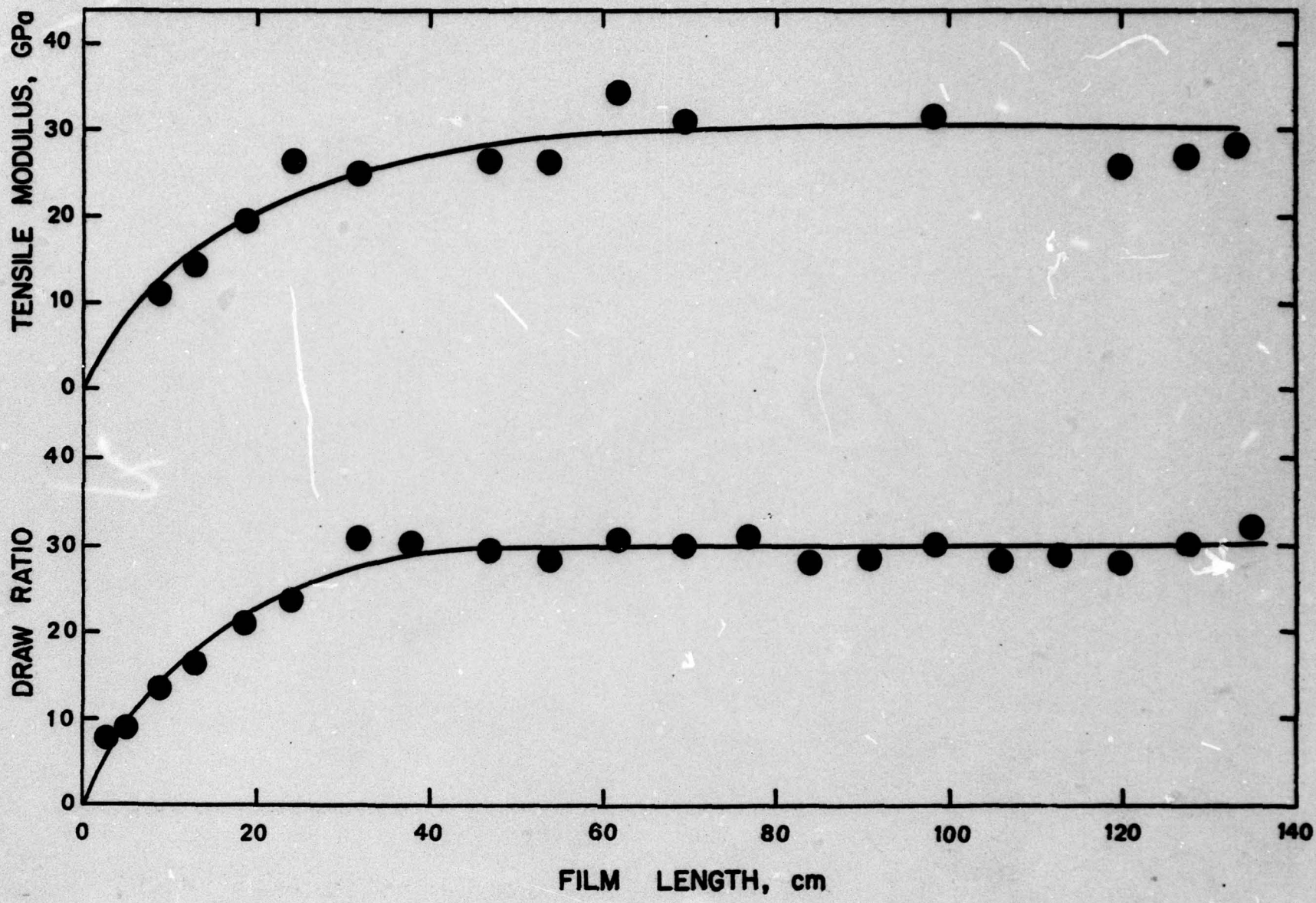


Figure 2


TENSILE MODULUS, GPa
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30
20
10
0
DRAW RATIO
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30
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0
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60
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140
FILM LENGTH, cm

Figure 3

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